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The liquid structure of Sn-based lead-free solders and the correlative effect in liquid-solid interfacial reaction

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Abstract. Two lead-free solder alloys, Sn-0.7Cu and Sn-2Cu (wt.%), have been examined using X-ray diffraction method. The liquid structure of Sn-0.7Cu is similar to that of pure Sn. A pre-peak has been found in the low Q part on the structure factor S(Q) for Sn-2Cu tested under 260°C, but it disappeared finally when the testing temperature reached 400°C. The interfacial reactions between liquid solders and Cu substrates at 260°C were also studied. The results show that the IMC layer at Sn-2Cu/Cu joint is thicker than that at Sn-0.7Cu/Cu interface. The correlative effect of liquid structure on phase evolution in the solder joints are analyzed and discussed.

1. Introduction
The structure and properties of liquid metals have a great impact on those of metallic solids obtained by solidification of melts [1,2]. It was realized that there is short-range order (SRO) in metallic melt since X-ray diffraction method has been used to explore the liquid structure [3]. While Bian et al. have found that there exits not only SRO but also medium-range order (MRO) in liquid metals [4].

Eutectic Sn-0.7Cu solder has been recommended as a promising lead-free solder, and has been widely used in wave soldering and flip chip applications [5-7]. During soldering process, the molten solder will react with the Cu substrate, and then intermetallic compounds (IMCs) will be formed at the interface. The rate of such interfacial reaction and the thickness of the interfacial IMC layer play a very important role on the performance of the packaging and on the reliability of the component in service. As the interfacial reaction occurs between molten solder and solid substrate, so the liquid structure of solder must has significant effect on the reaction and the formation of interfacial product. However, the work about liquid structure of molten solder hasn’t been carried out yet. In this paper, the liquid structure of Sn-0.7Cu and Sn-2Cu solders was studied by using X-ray diffraction. The
correlative effect of the liquid structure on the interfacial reaction between solders and Cu substrates was then discussed.

2. Experimental procedure
The Sn-0.7Cu and Sn-2Cu solder alloys used in this work were obtained by melting high purity elements in a vacuum furnace at 600°C for 5 h under argon atmosphere. X-ray diffraction measurements were performed using a θ–θ type liquid metal X-ray diffractometer. The Ashcroft–Langreth structure factor $S(Q)$ was obtained from the scattering intensity [8-13]. The pair distribution function $g(r)$ and the radial distribution function RDF were obtained from $S(Q)$ through the Fourier transformation. The solder joints were obtained by reflowing small solder sheets on Cu substrates at 260°C for 10, 60, 300s. To examine the IMCs formed at interface, SEM (scanning electron microscopes, JSM-5600LV) were performed. The average thickness of IMC layer was measured by using image analysis software (Q500IW).

3. Results and discussion

![Figure 1](image1.png)
Figure 1. The structure factor $S(Q)$ at different temperatures from the bottom up denotes 260°C, 330°C, and 400°C, respectively: (a) Sn-0.7Cu and (b) Sn-2Cu.

![Figure 2](image2.png)
Figure 2. Patterns of the pair distribution function $g(r)$ of Sn-Cu solders at different temperatures: (a) Sn-0.7Cu and (b) Sn-2Cu.

Figure 1 shows the total structure factor $S(Q)$ of liquid Sn-Cu solders as a function of $Q$ at different temperatures which from the bottom up denotes 260, 330, and 400°C, respectively. The top right corner of each figure is an enlargement of $S(Q)$ in the low $Q$ part. In the case of Sn-0.7Cu solder, the $S(Q)$ before the main peak presents a parabolic shape and no pre-peak can be detected. While for Sn-2Cu, a pre-peak appears in the low $Q$ part of $S(Q)$ tested under 260°C, and can be seen more clearly in the enlargement view, as shown in figure 1b. Since the pre-peak on $S(Q)$ represents there exist MRO structures in the melt, then it can be concluded that there exists MRO in liquid Sn-2Cu solder. However, the pre-peak broadens and decreases its intensity with increasing temperature and disappears finally when the testing temperature reaches 400°C.

Bian et al. has found that the presence of MRO structure in the molten metals is related to the content of alloy composition and closely related to the relevant phase structure in solid metals, and is also closely related to temperature [4]. As Cu₅Sn₆ is the dominant IMC that exists in solid Sn-Cu matrixes, the pre-peak in liquid Sn-2Cu can be attributed to the Cu₅Sn₆-phase-like clusters. The pre-peak disappeared finally at 400°C indicates this temperature is high enough to destroy the bond energy of the Cu-Sn clusters in liquid Sn-2Cu. Due to the content of Cu in eutectic Sn-0.7Cu solder is lower than the solubility limit of Cu in pure Sn (1.61wt.% at 250°C), strong interaction between Sn and Cu is hard to achieve in liquid Sn-0.7Cu so that no pre-peak can be detected.
Figure 2 gives the patterns of the pair distribution function \( g(r) \) of Sn-0.7Cu and Sn-2Cu at different temperatures, respectively. It can be seen in figure 2a that small shoulder peaks as marked by arrows exist on both sides of the main peaks. Qin et al. also found such shoulder peak on the \( g(r) \) of pure Sn [14]. No shoulder peak is detected on the \( g(r) \) of Sn-2Cu solder at 260°C, as shown in figure 2b. However, as the temperature increases, the shoulder peak appears on the right side of the main peaks for 330 and 400°C, respectively. In molten Sn-0.7Cu, there is no MRO and its liquid structure is similar to that of pure Sn. While for Sn-2Cu solder the Cu\textsubscript{6}Sn\textsubscript{5}-phase-like clusters at 260°C have a great contribution to the liquid structure. Nevertheless, Cu-Sn clusters are broken when the temperature goes higher, then the \( g(r) \) of Sn-2Cu at 330 and 400°C exhibit the same tendency to those of Sn-0.7Cu.

The RDF curves were decomposed by Gaussian peaks [15]. Figure 3 shows the sample of the Gaussian decomposition (three peaks) at 260°C. According to the study of Schnyders et al [16], for the Sn-Cu solders, the first, second, and third Gaussian peak are certainly Cu-Cu, Sn-Sn, and Cu-Sn correlations, respectively. The values of \( A \) in each analysis of Gaussian decomposition are listed in table 1. \( A_f \), \( A_s \), and \( A_t \) represent the area of first, second, and third Gaussian peak, respectively. The ratio of \( A_t/A_f \) for Sn-2Cu at each temperature is much larger than that for Sn-0.7Cu, which demonstrates the Cu-Sn correlations are much more prevalent in liquid Sn-2Cu solder.

<table>
<thead>
<tr>
<th>Solder</th>
<th>Temperature (°C)</th>
<th>( A_f )</th>
<th>( A_s )</th>
<th>( A_t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-0.7Cu</td>
<td>260</td>
<td>1.475</td>
<td>5.011</td>
<td>4.484</td>
</tr>
<tr>
<td></td>
<td>330</td>
<td>1.526</td>
<td>4.740</td>
<td>4.583</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>1.502</td>
<td>4.438</td>
<td>4.744</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>0.495</td>
<td>2.967</td>
<td>7.416</td>
</tr>
<tr>
<td>Sn-2Cu</td>
<td>330</td>
<td>0.801</td>
<td>2.552</td>
<td>7.367</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.568</td>
<td>2.874</td>
<td>7.639</td>
</tr>
</tbody>
</table>

The interfacial microstructure of solder joints reacted for 300s is given in figure 4. Cu\textsubscript{6}Sn\textsubscript{5} IMC layer is formed at each interface. It is found that the IMC layer formed at Sn-2Cu/Cu joint is thicker than that at Sn-0.7Cu/Cu. The size of Cu\textsubscript{6}Sn\textsubscript{5} “grain” at Sn-2Cu/Cu interface is also larger than those at Sn-0.7Cu/Cu, which indicates that the ripening process [17] of IMC grains is accelerated by higher Cu content in the solder. Figure 5 shows the relationship between the thickness (T) of interfacial IMC
layer and soldering time (t) plotted in lnT-ln$t$ format. T has a good linear relationship with t. During soldering Cu was dissolved fast into the molten solder from the substrate. But in the very early stage of soldering, Cu concentration in liquid Sn-0.7Cu solder near the interface didn’t meet the solubility limit, so the interfacial reaction would not occur at that time. However, when Sn-2Cu was soldered with Cu, the Cu$_6$Sn$_5$-phase-like MRO clusters have already formed as soon as the solder melted down. The MRO would then take part in the interfacial reaction to form IMC layer. As a result, the IMC layer formed in Sn-2Cu/Cu joint is thicker than that in Sn-0.7Cu/Cu.

4. Conclusions
Liquid structure of Sn-0.7Cu and Sn-2Cu solders is studied by X-ray diffraction method. A pre-peak has only been found in the low Q part on S(Q) of Sn-2Cu, but it disappears finally when the testing temperature reaches 400ºC. The appearance of the pre-peak is due to the existence of medium-range order (MRO) with Cu$_6$Sn$_5$-phase-like clusters in molten solder. The analysis of Gaussian decomposition of RDF demonstrates that the Cu-Sn correlations are much more prevalent in liquid Sn-2Cu solder. The MRO in liquid solder quickens the formation of interfacial IMC in the very early stage of soldering process and also accelerates the ripening process of IMC “grains” at the interface.

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References